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A Coupled-Cluster Study of the Molecular Structure, Vibrational Spectrum, and Heats of Formation of $XONO_2$ (X = H, F, Cl)

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The equilibrium structures, harmonic vibrational frequencies, dipole moments, and IR intensities of nitric acid, fluorine nitrate, and chlorine nitrate have been investigated by using the singles and doubles coupled-cluster method that also includes a perturbational estimate of the effects of connected triple excitations, CCSD(T). A standard triple-ζ double-polarized basis set was utilized. The equilibrium geometries and vibrational spectra of $HONO_2$ and $ClONO_2$ are shown to be in excellent agreement with the available experimental data. The *ab initio* vibrational spectrum of $FONO_2$ is also shown to be in excellent agreement with experiment. Unlike the FOOF and FON molecules, but similar to the *cis*- and *trans*-FONO molecules, $FONO_2$ is shown to possess normal bond distances. The bonding in $FONO_2$ is shown to be more similar to that in $ClONO_2$ than that in $HONO_2$, although there are still significant differences, especially in the partial atomic charges as deduced from Mulliken populations. This causes $FONO_2$ to possess almost no dipole moment, which is very different to both $HONO_2$ and $ClONO_2$. By using large atomic natural orbital basis sets, CCSD(T) energies are computed for four isodesmic reactions in order to determine an accurate heat of formation for $FONO_2$. Our best estimate for $\Delta H^\circ_{f,298}(FONO_2)$ is 3.1 ± 2.0 kcal/mol, indicating that the F−ONO_2 bond energy is 31.3 kcal/mol.

Introduction

There is growing interest in developing a more complete understanding of atmospheric chemistry. This interest is driven by various factors: (1) the need to develop effective alternatives to chlorofluorocarbons (CFCs); (2) the responsibility to determine the effect that man has on the global environment and to ensure that this effect does not lead to irrevocable harm to the global environment; (3) the desire simply to gain a detailed understanding of the complicated workings of earth's atmosphere. The present study is aimed at yielding a more detailed characterization of the ground electronic states of the $XONO_2$ (X = H, F, and Cl) molecules. Nitric acid and chlorine nitrate are known to be significant components of the stratosphere.[1] Indeed, $ClONO_2$ is thought to be one of the two major reservoir species for Cl, the other being HCl. As such, there have been numerous experimental and *ab initio* studies of $HONO_2$ and $ClONO_2$ over the past several years, investigating molecular structures, microwave, vibrational, and electronic spectra, photodissociation mechanisms, and heterogeneous reactions on polar stratospheric clouds (for example, see refs 2−28 and references therein). While the ground electronic states of $HONO_2$ and $ClONO_2$ are reasonably well characterized at this point, accurate quadratic force fields have not yet been determined. Evaluation of an accurate experimental force field is complicated by the number of degrees of freedom, thus requiring a substantial amount of data. On the other hand, *ab initio* methods have now reached the point where very accurate potential force fields may be determined for species such as the $XONO_2$ nitrates (see ref 29, for example). In the present study, accurate quadratic force fields are determined for $HONO_2$ and $ClONO_2$ using the singles and doubles coupled-cluster method that incorporates a perturbational estimate of the effects of connected triple excitations,[30] CCSD(T), in conjunction with a triple-ζ double-polarized (TZ2P) one-particle basis set. The reliability of these force fields is demonstrated by comparison of the CCSD(T)/TZ2P equilibrium structures and vibrational spectra to experimental quantities.

The situation for fluorine nitrate is somewhat different, as the gas-phase vibrational spectrum is well-known,[12] but an accurate molecular geometry has not been determined experimentally. Pauling and Brockway[3] have determined an approximate molecular structure for $FONO_2$, but it is well established that at least one of the assumptions used in their analysis of electron diffraction experiments is incorrect. This is discussed in more detail later. There have been *ab initio* calculations (see refs 7 and 10 and references therein) of the molecular structure of $FONO_2$, but in comparison to CCSD(T)/TZ2P, these have used relatively low levels of theory. The heat of formation of $FONO_2$ is also not known very accurately.[1,31] Indeed, the recommended value[1] for use in stratospheric modeling has an uncertainty of ±7 kcal/mol! Thus, the present study provides accurate values for the molecular structure, the quadratic force field, and the heat of formation of $FONO_2$. Again, the reliability of the CCSD(T)/TZ2P molecular geometry and quadratic force field is demonstrated by comparison of the *ab initio* and experimental vibrational frequencies.

In addition to reporting accurate molecular parameters for the $XONO_2$ (X = H, F, and Cl) compounds, qualitative aspects of the bonding in these nitrates are compared and contrasted. It is shown that the X = F and Cl compounds have more similar bonding relative to X = H, although even these two compounds exhibit significant differences in the distribution of partial atomic charges. Differences in the bonding for the $XONO_2$ molecules are attributed primarily to the different atomic hydrogen, fluorine, and chlorine electronegativities. In the next section, the computational methods used in the present study are described. The following section contains our results and discussion. Conclusions are presented in the final section.

Computational Methods

The equilibrium geometries were determined with a TZ2P basis set at the CCSD(T) level of theory. The TZ2P basis set

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used here for the H, O, N, F, and Cl atoms has been described in detail previously.[9,32,33] All six components of the Cartesian d functions were included in the basis set. Coupled-cluster analytical gradient methods[34,35] were used to locate equilibrium structures, while quadratic force constants, harmonic frequencies, and IR intensities were determined by finite differences of analytical gradients. The dipole moment was determined as the derivative of the energy with respect to an external electric field. The dipole moment was determined as the derivative of the energy with respect to an external electric field. In all coupled-cluster and MP2 calculations, the O, N, and F 1s-like core molecular orbitals and the Cl 1s, 2s, and 2p molecular orbitals were constrained to be doubly occupied in all configurations (i.e., the frozen core approximation was used). In addition, the O, N, F, and Cl 1s core-counterpart virtual molecular orbital was deleted from the TZ2P basis coupled-cluster calculations.

In order to determine an accurate heat of formation for $FONO_2$, isodesmic reaction energies have been evaluated at the MP2, CCSD, and CCSD(T) levels of theory using very large ANO basis sets.[36] These ANO basis sets have also been described in detail previously.[32,33] The basis set denoted ANO1 consists of 5s4p2d, 4s3p2d, and 4s2p ANOs on Cl (O, N, and F) and H, respectively. The ANO2 basis set is composed of 5s4p2d1f, 4s3p2d1f, and 4s2p1d ANOs on Cl (O, N, and F) and H. For the ANO basis sets, only the spherical harmonic components of the d- and f-type functions were included.

The coupled-cluster geometry optimizations were performed with the TITAN[37] program system. The MP2 and coupled-cluster single-point energies were performed with the TITAN coupled-cluster programs interfaced to the SEWARD[38] integral program, and the SWEDEN[39] self-consistent-field and transformation programs. All calculations were performed on either the Computational Chemistry Branch's Convex C210 computer or the NASA Ames Central Computer Facility's Cray C90.

Results and Discussion

A. Equilibrium Structures and Dipole Moments. Table 1 contains the CCSD(T)/TZ2P equilibrium structures, dipole moments, rotational constants, and T_1 diagnostics[40] of $HONO_2$, $FONO_2$, and $ClONO_2$, together with the available experimental data. Refer to Figure 1 for the labeling of the oxygen atoms. Note that in all cases the experimental data refer to vibrationally averaged parameters. Keeping this in mind, the agreement between theory and experiment for the geometry of $HONO_2$ is very good, with the largest deviation occurring for r_{ON}. The agreement between theory and experiment for the dipole moment of nitric acid is also excellent. For $FONO_2$, an approximate experimental structure was obtained from analysis of electron diffraction experiments in 1937 by Pauling and Brockway.[3] Electron diffraction experiments are often unreliable for highly accurate molecular geometries, and moreover, the purpose of Pauling and Brockway's experiments was to determine a qualitatively correct structure and to test the "Adjacent Charge Rule" with regard to resonating Lewis dot structures. Taking these aspects into consideration, the agreement with the CCSD(T)/TZ2P calculations is quite reasonable, if not quantitative. It should be noted, however, that the difference for the O–N bond distance is quite large (0.125 Å) and that the CCSD(T)/TZ2P value is most certainly more accurate. Indeed, it is expected that the CCSD(T)/TZ2P equilibrium structure for $FONO_2$ is the most accurate available.

Pauling and Brockway also suggested that $FONO_2$ was nonplanar, with the F–O bond in a plane that bisects the O_1NO_2 angle. This type of structure for $FONO_2$ also has C_s symmetry, although the number of a′ and a″ vibrational modes in the planar and nonplanar C_s structures is different. There has been much debate over the years concerning the planarity or nonplanarity of halogen nitrates, such as $FONO_2$ and $ClONO_2$, with strong arguments on both sides.[5,6,41,42] However, it is now generally agreed[5–7,9,41] that both $FONO_2$ and $ClONO_2$ possess planar structures, and thus, only the planar structures have been investigated here. Moreover, the agreement between CCSD(T)/TZ2P and experiment for the geometries of $HONO_2$

TABLE 1: Total Energies (E_h), Equilibrium Structures, Rotational Constants (MHz), and Dipole Moments (D) of $XONO_2$[a]

	$HONO_2$		$FONO_2$		$ClONO_2$	
	CCSD(T)	expt[b]	CCSD(T)	expt[c]	CCSD(T)	expt[d]
E	0.442 760		0.426 191		0.464 060	
τ_1[e]	0.020		0.021		0.021	
μ	2.19	2.17	0.11		1.08	0.77
r_{XO}	0.969	0.964	1.428	1.42	1.707	1.673
r_{ON}	1.418	1.406	1.515	1.39	1.511	1.499
r_{NO_1}	1.216	1.211	1.188	1.29	1.195	1.196
r_{NO_2}	1.200	1.199	1.196	1.29	1.197	1.196
$\angle XON$	101.5	102.2	106.2	105	111.9	113.0
$\angle ONO_1$	115.4	115.9	117.2		117.8	118.6
$\angle ONO_2$	114.0	113.9	107.8		108.7	108.8
A_e	12909	13011	12007		11981	12106
B_e	11992	12100	4525		2723	2777
C_e	6217	6261	3286		2218	2258

[a] The energy is reported as $-(E + 280)$ for $HONO_2$, $-(E + 379)$ for $FONO_2$, and $-(E + 739)$ for $ClONO_2$. Obtained with the TZ2P basis set. Bond lengths in Å and angles in deg. See Figure 1 for labeling of atoms. [b] Vibrationally averaged structure, dipole moment, and rotational constants from ref 2. [c] Approximate structure from ref 3; they also give the O_1NO_2 angle as 125°, compared with the CCSD(T)/TZ2P value of 135.0°. [d] Vibrationally averaged structure from ref 4; vibrationally averaged dipole moment from ref 5; vibrationally averaged rotational constants from ref 6. [e] The τ_1 diagnostic is based on the norm of the T_1 amplitudes in the CCSD wave function, and it has been shown to give a good indication of the reliability of results from single-reference-based electron correlation procedures. A value larger than 0.02 has been suggested as indicating that results from single-reference-based correlation procedures limited to single and double excitations (e.g., CCSD) should be viewed with caution. CCSD(T) has been shown to perform well for τ_1 values as large as 0.06–0.08. See refs 29 and 40 for a more complete discussion of the τ_1 diagnostic.

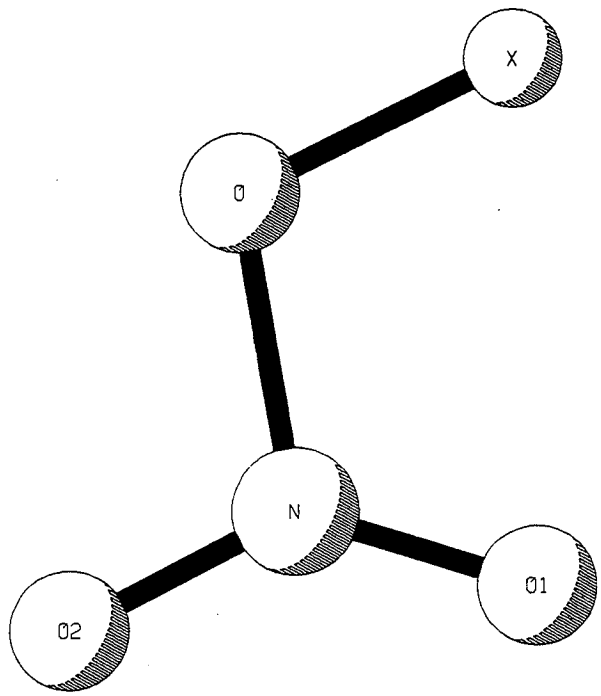

Figure 1. Depiction of the planar $XONO_2$ structure.

and $ClONO_2$ (see discussion below) and also the agreement between CCSD(T)/TZ2P and experiment for the vibrational spectra of $HONO_2$, $FONO_2$, and $ClONO_2$ lend strong support for the planarity of the $FONO_2$ and $ClONO_2$ structures. Interestingly, according to the CCSD(T)/TZ2P calculations, both $FONO_2$ and $ClONO_2$ possess considerably smaller dipole moments than found for $HONO_2$, especially $FONO_2$. This is no doubt one reason that an accurate gas-phase experimental structure of $FONO_2$ has not yet been determined.

After the submission of this paper, the results of a new experimental investigation of the molecular structure of $FONO_2$ appeared (Casper, B.; Dixon, D. A.; Mack, H.-G.; Ulic, S. E.; Willner, H.; Oberhammer, H. *J. Am. Chem. Soc.* **1994**, *116*, 8317). The agreement between the present CCSD(T)/TZ2P structure and the new experimental one is very good for those parameters determined. That is, in the analysis of the experimental structure, the r_{NO_1} and r_{NO_2} values were assumed to be the same, which the CCSD(T)/TZ2P results in Table 1 show not to be a great assumption for $FONO_2$. Hence, it is likely that a better "experimental" structure could be obtained by incorporating some of the CCSD(T)/TZ2P data contained herein.

The CCSD(T)/TZ2P structure for $ClONO_2$ has been presented previously,[9] although the vibrationally averaged experimental structure[4] was not available at that time. Vibrationally averaged rotational constants[6] were used for comparison, however. The agreement between the CCSD(T)/TZ2P equilibrium rotational constants and the vibrationally averaged experimental values is very good. The agreement between experiment and theory is good for the molecular structure also. The largest discrepancy occurs for the Cl–O bond distance which is probably mainly due to deficiencies in the TZ2P basis set. Nonetheless, the differences between experiment and the CCSD(T)/TZ2P equilibrium structure are well within the combined uncertainties. On the other hand, the agreement between theory and experiment for the dipole moment is only fair. Given the agreement between the CCSD(T)/TZ2P level of theory and experiment for the dipole moments of other molecules, including some chlorine species,[29] it seems unlikely that the CCSD(T)/TZ2P level of theory could be in error by 0.3 D. It also seems unlikely that this discrepancy could be due to the effects of vibrational averaging, and therefore, the CCSD(T)/TZ2P value indicates that a more accurate experimental determination is needed. It is hoped that the accurate CCSD(T)/TZ2P equilibrium structures of $FONO_2$ and $ClONO_2$ will aid in the analysis of future experiments and in the complete experimental characterization of the ground electronic states of these species.

In comparing analogous geometrical parameters between the $XONO_2$ molecules, some significant differences are found. The r_{ON} bond distance is far shorter for $HONO_2$ than for either $FONO_2$ or $ClONO_2$. In fact, it is almost 0.1 Å shorter for $HONO_2$. While the range of the r_{NO_1} and r_{NO_2} bond distances is considerably smaller, the values are nonetheless consistent with the O–N bonding trend. That is, these bonds are shorter for $FONO_2$ and $ClONO_2$ than for $HONO_2$. These differences in the nitrogen–oxygen bond distances suggest that the $N-O_1$ and $N-O_2$ bonds are stronger in the $FONO_2$ and $ClONO_2$ compounds relative to $HONO_2$ and that the O–N bond is weaker. Diagonal quadratic force constants presented later support this conclusion. The two other geometrical parameters that exhibit large differences between the three species are the XON and ONO_2 bond angles. The XON bond angle is clearly correlated with the size of the X atom, being smallest for H and largest for Cl, with the F value being almost halfway between. The value of the ONO_2 angle, however, appears to correlate better with the magnitude of the O–N bond distance

TABLE 2: Harmonic Frequencies (cm^{-1}) and IR Intensities (km/mol) of $XONO_2$[a]

	$HONO_2$		$FONO_2$		$ClONO_2$	
	CCSD(T)	expt[b]	CCSD(T)	expt[c]	CCSD(T)	expt[b]
$\omega_1(a')$	3747(85)	3550 m	1760(380)	1759 vs	1730(343)	1735 vs
$\omega_2(a')$	1722(345)	1710 vs	1308(210)	1301 vs	1298(254)	1292 vs
$\omega_3(a')$	1349(207)	1326 s	939(19)	928 s	813(164)	809 s
$\omega_4(a')$	1310(162)	1304 vs	818(150)	804 s	786(18)	780 ms
$\omega_5(a')$	895(154)	879 s	634(5.0)	633 vw	569(56)	560 s
$\omega_6(a')$	649(9.3)	647 w	460(23)	455 ms	434(14)	434 m
$\omega_7(a')$	580(9.3)	580 w	298(2.2)	303 vw	256(0.1)	270 vvw
$\omega_8(a'')$	761(9.5)	763 s	708(9.4)	709 m	713(9.0)	711 w
$\omega_9(a'')$	469(117)	458 m	144(0.1)	152 vvw	122(0.3)	120

[a] IR absorption intensities in parentheses. See text for discussion of the nature of the normal modes. [b] Fundamental frequencies from ref 11. [c] Fundamental frequencies from ref 12.

or, in other words, the distance between the O and O_2 atoms (which differs primarily due to the different r_{ON} bond distances). That is, the ONO_2 angle is largest for $HONO_2$, where the r_{ON} bond distance is smallest, and it is smallest for $FONO_2$, where the r_{ON} bond distance is largest, although the differences between the $FONO_2$ and $ClONO_2$ compounds are relatively modest. To summarize, the geometrical structures of the $FONO_2$ and $ClONO_2$ compounds are similar, while the structure for $HONO_2$ shows some significant differences—these differences may be attributed primarily to the different electronegativities and sizes of atomic hydrogen, fluorine, and chlorine. The bonding in the $XONO_2$ molecules is discussed further below.

B. Vibrational Frequencies and Quadratic Force Constants. Table 2 contains the CCSD(T)/TZ2P harmonic vibrational frequencies and IR intensities for $HONO_2$, $FONO_2$, and $ClONO_2$, together with the observed gas-phase fundamental vibrational frequencies.[11,12] The O–H stretch of nitric acid represents the only vibrational band that will have an appreciable anharmonic correction (i.e., greater than 50 cm^{-1}). The average of the anharmonic correction[43] for the O–H stretches in H_2O is 181 cm^{-1}—using this value to correct the CCSD(T)/TZ2P O–H harmonic frequency in $HONO_2$ brings it into very good agreement with the experimental fundamental. The agreement between CCSD(T)/TZ2P and experiment for all of the other bands of $HONO_2$ and for all of the vibrational bands of $FONO_2$ and $ClONO_2$ is excellent, demonstrating the quality of the CCSD(T)/TZ2P level of theory for these nitrates. While anharmonic corrections will change the *ab initio* values somewhat, aside from the O–H stretch discussed above, it is expected that the anharmonic correction for all of the other vibrational bands contained in Table 2 will be less than 30 cm^{-1}, and in most cases less than 10 cm^{-1}. Hence, the excellent agreement between experiment and the CCSD(T)/TZ2P harmonic frequencies is not fortuitous.

Performing potential energy distribution analyses on the CCSD(T)/TZ2P quadratic force fields shows that in general there is considerable mixing between the various molecular motions, particularly for the a′ frequencies below 900 cm^{-1}. The O–H stretch ($HONO_2$; 3747 cm^{-1}) and the antisymmetric (1722, 1760, and 1730 cm^{-1} for $HONO_2$, $FONO_2$, and $ClONO_2$, respectively) and symmetric (1310, 1308, and 1298 cm^{-1}, respectively) combinations of the NO_1 and NO_2 stretches are straightforwardly identified for all three molecules. These descriptions are in qualitative agreement with those given in the experimental assignments.

A qualitative description of the IR intensity is also given in the experimental tabulations.[11,12] Comparing these with the CCSD(T)/TZ2P IR intensities given in Table 3 shows good agreement for the bands with very small intensities and also for most of the bands with very large intensities. The one

exception to the latter situation concerns the 1349 and 1310 cm^{-1} bands of $HONO_2$, where the experimental observations indicate that the band at 1349 cm^{-1} is "strong", whereas the band at 1310 cm^{-1} is denoted as "very strong". Considering that these bands are so close together and that the CCSD(T)/TZ2P IR intensities have been determined via the double harmonic approximation, it seems likely that the effects of anharmonicity are the primary cause for the error in the calculated values. There are a couple of other examples where the CCSD(T)/TZ2P relative IR intensities do not match the experimental observations: for example, the 939 and 460 cm^{-1} bands in $FONO_2$ and the 786 and 434 cm^{-1} bands in $ClONO_2$. Of the molecular properties included in this study, it has been shown[44] that IR intensities are the most sensitive to the level of theory employed. However, the effects of anharmonicity can also be large[45] and may result in changing the relative ordering of band intensities, so the most likely cause of the discrepancy for the latter examples is not evident.

Given the excellent agreement between theory and experiment for the vibrational frequencies of $HONO_2$, $FONO_2$, and $ClONO_2$, the CCSD(T)/TZ2P quadratic force constants are expected to be of high accuracy. Hence, they are presented in Table 3 using the internal coordinate definitions given below:

$$S_1(a') = r_{XO} \quad (1.1)$$

$$S_2(a') = r_{ON} \quad (1.2)$$

$$S_3(a') = \frac{1}{2^{1/2}}(r_{NO_1} + r_{NO_2}) \quad (1.3)$$

$$S_4(a') = \frac{1}{2^{1/2}}(r_{NO_1} - r_{NO_2}) \quad (1.4)$$

$$S_5(a') = \angle XON \quad (1.5)$$

$$S_6(a') = \angle ONO_1 \quad (1.6)$$

$$S_7(a') = \angle ONO_2 \quad (1.7)$$

$$S_8(a'') = \tau_{XONO_1} \quad (1.8)$$

$$S_9(a'') = \tau_{XONO_2} \quad (1.9)$$

where τ represents a torsion angle. Force constants for the $N-O_1$ and $N-O_2$ stretches are given as the symmetric and antisymmetric combination since analysis of the normal mode eigenvectors shows this to be a very good description of the bands occurring near 1310 and 1730 cm^{-1}, respectively. As indicated previously, note that the f_{22} force constant is largest for $HONO_2$ while the f_{33} and f_{44} force constants are smallest for $HONO_2$. Excluding force constants involving the S_1 internal coordinate, the quadratic force constants for $FONO_2$ and $ClONO_2$ are generally very similar, while those for $HONO_2$ often exhibit significant differences relative to the halogen nitrates. This observation is consistent with the earlier discussion comparing the geometrical structures of the $XONO_2$ compounds.

C. Bonding and Heats of Formation. Additional insight into the difference of the bonding in the $XONO_2$ compounds may be gained by comparing the CCSD(T)/TZ2P Mulliken populations for the three nitrates. These are presented in Table 4. The N atom has about the same large positive partial charge for all three molecules, and the negative partial charges for the O_1 and O_2 atoms (see Figure 1) are fairly consistent for the three molecules, being somewhat larger in magnitude for $HONO_2$ and somewhat smaller for $FONO_2$. The partial charges on the X and O atoms, however, vary greatly among the three $XONO_2$ species. The H and Cl atoms both have positive partial charges, with the charge on H being about twice that for Cl. Conversely, the F atom has a negative partial charge—the surprising aspect here is the small magnitude of this negative partial charge, which is due to the electron-withdrawing ability of the NO_3 moiety. The central O atom partial charge is very negative for $HONO_2$, less negative for $ClONO_2$, and slightly positive for $FONO_2$. To summarize, the difference in atomic partial charges between the $XONO_2$ compounds, as given by Mulliken population analyses, is directly correlated to the difference in the X atom electronegativities, and the difference in atomic partial charges leads to vastly different molecular dipole moments for the $XONO_2$ species. The Mulliken populations in Table 4 also suggest that the $FONO_2$ compound is not that stable since there is one instance where the partial charge on adjacent atoms is of the same sign, and this occurs for the lowest energy dissociation channel (i.e., the $FO-NO_2$ bond; see later discussion). Indeed, Pauling and Brockway[3] found gas-phase $FONO_2$ to explode at room temperature.

The heats of formation of $HONO_2$ and $ClONO_2$ are both known to high accuracy (32.10 ± 0.10 and 6.3 ± 0.2 kcal/mol for $HONO_2$ and $ClONO_2$, respectively) from experiment,[31,46] while the uncertainty in the experimental heat of formation of $FONO_2$ is quite large (e.g., see refs 1 and 31). Therefore, it is of interest to determine a more reliable value for the heat of formation of $FONO_2$, and the best approach involves the use of a combination of experimental and *ab initio* data. That is, due to a cancellation of errors, *ab initio* methods generally perform very well in determining the enthalpy of an isodesmic reaction. The key, then, is to set up an isodesmic reaction where the experimental heats of formation of all species, except for the molecule of interest, are known very accurately. Unfortu-

TABLE 3: Quadratic Force Constants of $XONO_2$ Obtained at the CCSD(T)/TZ2P Level of Theory[a]

	$ClONO_2$	$FONO_2$	$HONO_2$		$ClONO_2$	$FONO_2$	$HONO_2$
f_{11}	3.2699	4.2364	7.8590	f_{36}	−0.6221	−0.5878	−0.4052
f_{12}	0.3894	0.2411	0.0286	f_{37}	−0.5773	−0.5070	−0.4563
f_{13}	0.0119	0.1078	−0.1155	f_{44}	9.6691	9.9564	9.1323
f_{14}	0.0063	0.0651	−0.0313	f_{45}	−0.2180	−0.2755	−0.0234
f_{15}	0.2568	0.1849	0.1597	f_{46}	0.3047	0.2781	0.6003
f_{16}	−0.1141	−0.1329	−0.1376	f_{47}	−0.4626	−0.4888	−0.4773
f_{17}	0.1540	0.2378	0.0297	f_{55}	1.5757	1.4643	0.9629
f_{22}	2.1309	2.1916	3.6812	f_{56}	0.2672	0.1508	−0.1064
f_{23}	1.0367	0.9826	1.3429	f_{57}	0.2116	0.2591	0.2278
f_{24}	−0.0930	−0.0981	0.0433	f_{66}	2.8212	2.6890	3.0059
f_{25}	0.5064	0.4282	0.3676	f_{67}	1.3590	1.3192	1.4797
f_{26}	0.7552	0.7610	0.6237	f_{77}	2.6414	2.5542	2.8823
f_{27}	0.6068	0.4614	0.7391	f_{88}	0.5447	0.5509	0.6108
f_{33}	12.4047	12.6337	11.8323	f_{89}	−0.5486	−0.5470	−0.5783
f_{34}	0.0361	0.2111	−0.5023	f_{99}	0.6576	0.6599	0.6532
f_{35}	0.0790	0.0390	0.1332				

[a] Units are aJ/Å^2, aJ/(Å·rad), and aJ/rad^2. See text for definition of the internal coordinates.

TABLE 4: Atomic Charge Distributions Based on Mulliken Population Analyses for $XONO_2$ at the CCSD(T)/TZ2P Level of Theory[a]

	$HONO_2$	$FONO_2$	$ClONO_2$
X[b]	+0.36	−0.08	+0.18
O	−0.33	+0.004	−0.22
N	+0.70	+0.70	+0.68
O_1	−0.39	−0.30	−0.33
O_2	−0.34	−0.32	−0.32

[a] See Figure 1 for labeling of atoms. [b] X = H, F, or Cl.

TABLE 5: Energies (kcal/mol) for the Isodesmic Reactions (2.1)−(2.4) (CCSD(T)/TZ2P Geometries Were Used)[a]

	ΔE_1	ΔE_2	ΔE_3	ΔE_4
MP2/ANO1	−3.6	−0.8	2.3	4.9
MP2/ANO2	−3.2	−0.8	3.5	5.3
CCSD/ANO1	1.8	−0.6	10.8	5.0
CCSD/ANO2	2.3	−0.7	12.1	5.4
CCSD(T)/TZ2P	−0.9	−0.8	6.6	5.4
CCSD(T)/ANO1	−0.8	−0.6	6.6	5.1
CCSD(T)/ANO2	−0.3	−0.6	7.9	5.5
ΔZPVE[b]	−1.4	0.1	−2.3	0.1
ΔVT[c]	0.6	−0.1	1.0	0.0

[a] Zero-point vibrational energies not included—see text for energy differences where these are included. [b] Zero-point vibrational energies determined using CCSD(T)/TZ2P harmonic frequencies. [c] Energy changes due to thermal population of vibrational energy levels at 298.15 K.

nately, it has been noted,[33,47,48] that there are some small inconsistencies in the experimental heats of formation of the fluorine and chlorine oxide species. Thus, in the present study, we use several isodesmic reactions in order to determine a "best estimate" for the $FONO_2$ heat of formation. The following isodesmic reactions have been investigated:

$$HONO_2 + HOF \rightarrow H_2O + FONO_2 + \Delta E_1 \quad (2.1)$$

$$ClONO_2 + HOF \rightarrow HOCl + FONO_2 + \Delta E_2 \quad (2.2)$$

$$2HONO_2 + F_2O \rightarrow H_2O + 2FONO_2 + \Delta E_3 \quad (2.3)$$

$$2ClONO_2 + F_2O \rightarrow Cl_2O + 2FONO_2 + \Delta E_4 \quad (2.4)$$

Single-point MP2, CCSD, and CCSD(T) energies have been evaluated for all of the species involved in reactions 2.1−2.4 using the ANO1 and ANO2 basis sets described earlier. In all cases, CCSD(T)/TZ2P geometries have been used. Table 5 contains a summary of the ΔE values obtained for reactions 2.1−2.4, together with contributions due to zero-point vibrational energies and the thermal population of vibrational energy levels. Except for reactions 2.1 and 2.3, the reaction energies show little dependence on the electron correlation method used, and none of the reaction energies exhibit a significant dependence on the one-particle basis set. The (T) triples contribution to ΔE_1 and ΔE_3 is still quite small, however, indicating that convergence with respect to the treatment of electron correlation has been achieved. Thus, based on the results presented in Table 5 and also based on experience,[29] the CCSD(T)/ANO2 reaction energies are expected to be accurate to better than ±0.5 kcal/mol. Taking the CCSD(T)/ANO2 reaction energies as our best estimate and correcting these for the effects of zero-point vibrational energy and thermal population of vibrational energy levels (298.15 K; see Table 5) yields −0.8, −0.6, 6.6, and 5.6 kcal/mol for ΔE_1, ΔE_2, ΔE_3, and ΔE_4, respectively. Combining these *ab initio* reaction energies with experimental heats of formation for $HONO_2$, H_2O, F_2O, and HOCl from ref 31, Cl_2O and $ClONO_2$ from ref 46, and HOF from ref 49 gives 4.3, 2.9, 3.0, and 2.3 kcal/mol for $\Delta H^\circ_{f,298}(FONO_2)$ from reactions 2.1 through 2.4, respectively. The range in these values is due to small errors in the experimental thermochemical data, which, as noted previously, are primiarly in the experimental heats of formation of fluorine and chlorine oxide species. Averaging these three values gives 3.1 kcal/mol, which is our best estimate for $\Delta H^\circ_{f,298}(FONO_2)$. Based on experience,[29] an uncertainty of ±2.0 kcal/mol is assigned, and it should be emphasized that the majority of this is due to the aforementioned errors in the experimental thermochemical data. It should also be noted that with this uncertainty the range in our best estimate for the $FONO_2$ heat of formation more than spans all of the values determined from the isodesmic reactions (2.1)−(2.4). Thus, the $\Delta H^\circ_{f,298}(FONO_2)$ value determined in this work, 3.1 ± 2.0 kcal/mol, has a considerably smaller uncertainty than previous quantities.[1,31]

It is now possible to determine an accurate enthalpy for the reaction

$$FONO_2 \rightarrow F + NO_3 \quad (2.5)$$

Combining our best estimate for $\Delta H^\circ_{f,298}(FONO_2)$ and the experimental[31,50] heats of formation for F and NO_3, a $\Delta H_{f,298}$ value of 31.3 kcal/mol is obtained, which indicates that the F−O bond in $FONO_2$ is rather weak compared to other F−O bonds such as F−OH (48.9 kcal/mol; $\Delta H^\circ_{f,298}$ value for OH taken from ref 31). This is consistent with the observations of Pauling and Brockway and also with the Mulliken populations discussed earlier.

Finally, it is of interest to examine the $XO-NO_2$ bond energies since this is the lowest energy dissociation pathway for these molecules. Using the heats of formation referenced above, our best estimate for $\Delta H^\circ_{f,298}(FONO_2)$, a recent determination[50] for ClO, and the JANAF[31] value for OF, $XO-NO_2$ bond energies of 49.3, 30.8, and 25.9 kcal/mol are obtained for X = H, F, and Cl, respectively. The much larger bond energy for X = H is consistent with the shorter r_{ON} bond relative to X = F or Cl. The significant difference between the $XO-NO_2$ bond energies for X = F and Cl, however, is not consistent with the relative geometrical structures nor with the Mulliken populations which suggest that the $ClO-NO_2$ bond energy will be larger than the $FO-NO_2$ bond energy. This discrepancy may be due to the large uncertainty[31] in the $\Delta H^\circ_{f,298}$ value for OF (±10.0 kcal/mol), and further investigation is warranted.

Conclusions

The CCSD(T)/TZ2P level of theory has been used to determine accurate equilibrium geometries, harmonic frequencies, dipole moments, and quadratic force fields for the $XONO_2$ (X = H, F, and Cl) molecules. The CCSD(T)/TZ2P structures for $HONO_2$ and $ClONO_2$ and the CCSD(T)/TZ2P vibrational spectra for all three molecules are in excellent agreement with experiment. The ab initio dipole moment of $HONO_2$ is also in very good agreement with experiment, but the theoretical dipole moment for $ClONO_2$ is in only fair agreement with experiment. It is suggested that a new experimental determination of this quantity is needed. Based on the agreement mentioned above, the CCSD(T)/TZ2P structure for $FONO_2$ is expected to be very reliable, and it is hoped that these new data will aid in the interpretation of new experiments.

The molecular structures and bonding for $FONO_2$ and $ClONO_2$ are shown to be more similar to one another than to $HONO_2$. Qualitative aspects of the bonding in these $XONO_2$ compounds are discussed based on the equilibrium bond lengths and also based on Mulliken population analyses. It is concluded that the primary reason for the differences in the bonding is due to the different electronegativities and sizes for atomic hydrogen, fluorine, and chlorine.

CCSD(T) calculations using large ANO basis sets have been used to determine the enthalpy of several isodesmic reactions in order to determine an accurate value for $\Delta H^\circ_{f,298}(FONO_2)$. Our best estimate for $\Delta H^\circ_{f,298}(FONO_2)$, 3.1 ± 2.0 kcal/mol, has a considerably smaller uncertainty than previous values. Using this new $FONO_2$ heat of formation, it is shown that the F−ONO_2 bond energy is 31.3 kcal/mol and the $FO-NO_2$ bond

energy is 30.8 kcal/mol. However, the latter bond energy seems inconsistent with the $ClO-NO_2$ bond energy and is suspect due to a large uncertainty in the experimental OF heat of formation.

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